Production, properties and catalytic hydrogenation of furfural to fuel additives and value-added chemicals

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ABSTRACT

As our high dependence on the supply of diminishing fossil fuel reserves raise great concerns in its environmental, political and economic consequences, utilization of renewable biomass as an alternative resource has become increasingly important. Along this background, furfural as a building block, offers a promising, rich platform for lignocellulosic biofuels and value-added chemicals. These include 2-methylfuran and 2-methyltetrahydrofuran, furfuryl alcohol, tetrahydrofurfuryl alcohol, furan, tetra-hydrofuran as well as various cyclo-products (e.g., cyclopentanol, cyclopentanone). The various production routes started from furfural to various fuel additives and chemicals are critically reviewed, and the current technologies for efficient production are identified. Their potential applications as well as the fuel properties of these products are discussed. Challenges and areas that need improvement are also highlighted in the corresponding area. In short, we conduct a comprehensive review of the strategies to produce furfural, new approaches and numerous possibilities to utilize furfural in industrial and laboratory sector for the production of fuel additives and value-added chemicals.

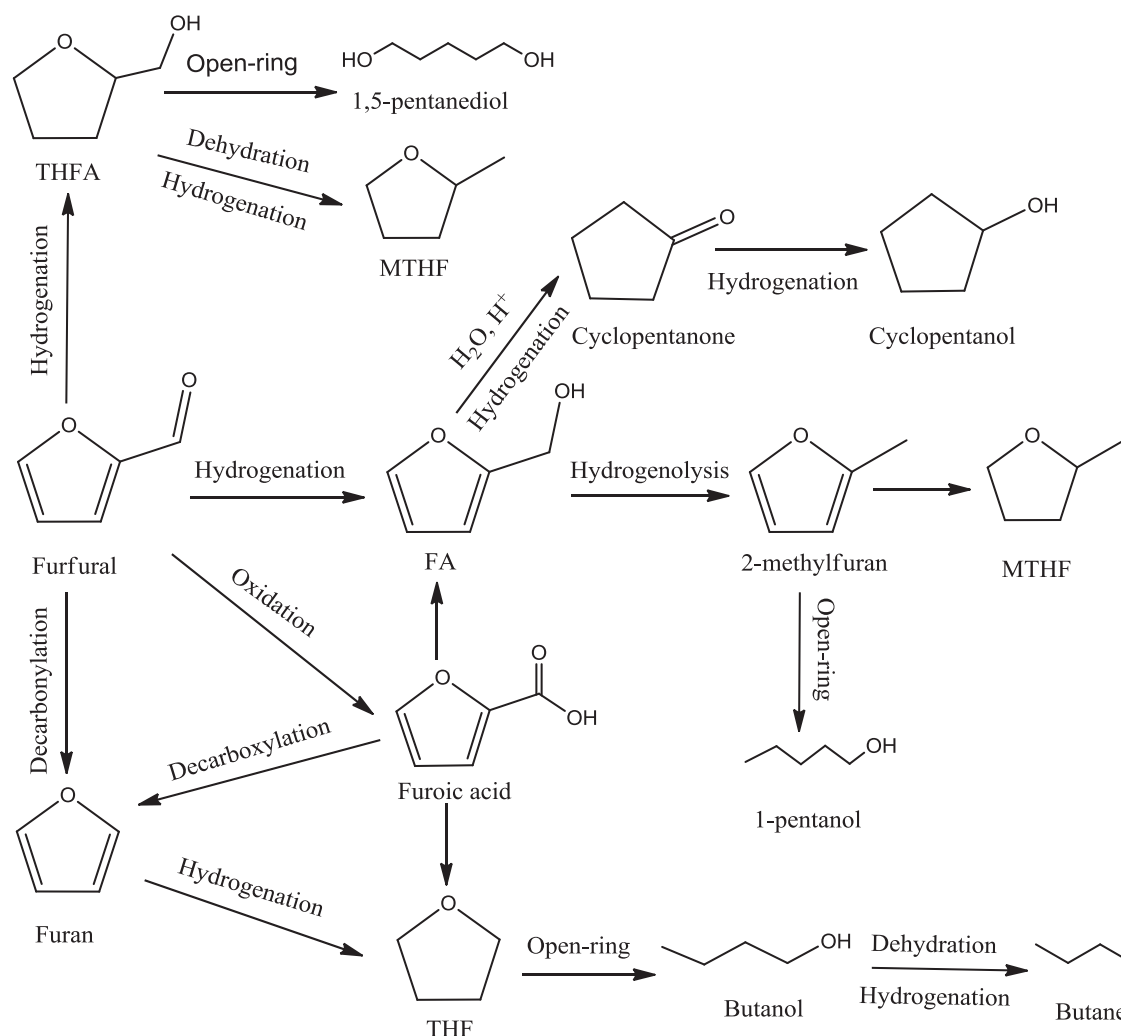© 2014 Elsevier Ltd. All rights reserved.

Contents

1. Introduction

Furfural, a sister chemical to 5-hydroxymethylfurfural, is one of the furan derivatives and is regaining attention as a biobased alternative for the production of everything from antacids and

Scheme 1. Production of furfural from hemicellulose.

fertilizers to plastics and paints [1–3]. Recently, it was identified as one of the most promising chemicals for sustainable production of fuels and chemicals in 21st century proposed by Bozell et al. [4]. It is the natural dehydration product of five-carbon sugars (e.g., arabinose and xylose) that are derived from hemicellulose biomass as shown in Scheme 1 [5,6]. The first time furfural produced in relatively large amounts was at the beginning of 1922 in the USA by the Quaker Oats Company, and the consequent development of furfural industry underwent quickly and achieved a relative maturity. As of 2002, the market price of furfural was reported to be ~$1700 per ton [7]. While in the June 2011, the prices were already in the order of $2000 per ton [8]. Apart from being a valuable platform chemical derived from renewable biomass feed-stocks [9,10], furfural is also the precursor for many furan-based chemicals and solvents [2,6,11–13]. With a global production of ~300 kton/y, furfural is currently the sole precursor of furyl (e.g., furfurals, furanones and furans) furfuryl (e.g., furfuryl alcohol and furfuryl acetate), furoyl (e.g., 2-furoyl chloride and furoylglycine), and furfurylidene compounds in the chemical industry [14–17]. In addition, furfural along with its sister molecule HMF, can serve as two building blocks for other potential transportation fuels including dimethylfuran and ethyl levulinate [2,6,14].

As the following sections demonstrated, furfural offers enor-mous prospects for the development of a biorefinery-based feed-stock for future fuel additives and chemicals. It is very promising to offer a whole new class of chemicals of the furan family that can be derived from biomass feedstock, with very well established chemistry that has been comprehensively studied. This review leans on invaluable earlier reviews on furfural manufacture and upgrade, starting with the pioneered book from Dunlop and Peters [18], the book from Zeitsch [2] and numerous reviews [19–26]. For the sake of length and cohesion, we focus on our research on the technologies of chemical production and catalytic hydrogena-tion of furfural to yield various fuel additives and value-added chemicals.

2. Physical and chemical properties

2.1. Physical properties

Furfural, also named as 2-furaldehyde or furfuraldehyde with a molecular formula of $C_5H_4O_2$ and a molecular weight of 96.08, has an aromatic odor reminiscent of almonds [2,3]. Its exceptional physical properties make this heteroaromatic aldehyde as a selective extractant [2,3,14]: (i) to remove aromatics from lubri-cating oils to improve the relationship of viscosity vs. temperature, (ii) to remove aromatics from diesel fuels to improve the ignition properties and (iii) to form cross-linked polymers [27,28]. Besides, it was also used as an effective fungicide [14]. It has been reported that furfural is particularly effective in inhibiting the growth of wheat smut through killing the fungus when the wheat is soaked for 3 h in a 0.05% aqueous solution of furfural [2,3].

Table 1
General physical property of furfural [2,3].

Molecular weight	96.08
Boiling point (°C)	161.7
Freezing point (°C)	−36.5
Density at 25 °C	1.16
Refractive index, n_D	
20 °C	1.5261
25 °C	1.5235
Critical pressure Pc (MPa)	5.502
Critical temperature T_c (°C)	397
Solubility in water, wt% (25 °C)	8.3
Organic solvent (e.g., diethyl ether)	∞
Dielectric constant at 20 °C	41.9
Heat of vaporization (liquid), (kJ/mol)	42.8
Viscosity, mPa·s, 25 °C	1.49
Heat of combustion at 25 °C (kJ/mol)	234.4
Enthalpy of formation (kJ/mol)	−151
Heat of vaporization (kJ/mol)	42.8
Surface tension at 29.9 °C, (mN/m)	40.7
Explosion limits (in air) (vol%)	2.1–19.3
Flash point (°C), tag closed cup	61.7
Autoignition temperature (°C)	315

The general physical properties of furfural are given in Table 1. Due to its unique and attractive properties, it has been widely utilized as a building block for the synthesis of fine chemicals, the sustainable production of fuel additives and value-added chemi-cals [2,3,29–31].

2.2. Chemical properties

Furfural holds two powerful and functional groups, an alde-hyde (C=O) and a conjugated system (C=C–C=C), making its role as a versatile building block for various applications. The aldehyde group (C=O) of furfural can undergo typical reactions like acetalization, acylation, aldol and Knoevenagel condensations, reduction to alcohols, reductive amination to amines, decarbony-lation, oxidation to carboxylic acids, and Grignard reactions [2,9,23,31,32]. The furan ring system (C=C–C=C) can go through alkylation, hydrogenation, oxidation, halogenation, open-ring and nitration reactions [2,24,33,34]. Due to the electron-withdrawing and space effect of carbonyl group, the furan ring of furfural is less accessible to the cleavage of hydrolytic ring.

In this review, we mainly focus on the various well-studied production routes (e.g., dehydration, hydrogenation, oxidation, condensation, open-ring and decarbonyl) from furfural to fuel additives as well as value-added chemicals as shown in Scheme 2. The current technologies for their productions are identified and their potential applications as well as the fuel properties are discussed. Challenges and areas that need improvement are also highlighted.

Scheme 2. Conversion of furfural to various value-added chemicals and biofuels.

3. Mechanism for furfural formation

Furfural production is generally carried out by the initial hydrolysis of hemicellulose-derived pentosans into monomeric pentoses, and their subsequent acid-catalyzed dehydration into furfural as shown in Scheme 3 [2,33,35–37]. Numerous studies (Table 2) have performed on the production of furfural. However, contradictory theories exist in literatures to explain the mechanism of furfural formation from xylose under different catalytic systems [35–37]. Different supporting evidence has been obtained in the elucidation of the theories, making the real nature of the dehydration mechanism a little ambiguous. Two classic schemes seeking to explore the dehydration mechanism have been proposed [35,36]. Furfural is produced through the dehydration of five-carbon sugars such as xylose and arabinose (as shown in Scheme 3), which are often obtained from the hemicellulose fraction of lignocellulosic biomass. This mechanism was proposed and depended largely on the role of the 1,2-enediol intermediate in the formation of furfural from xylose in aqueous acid solution [36].

The other mechanism was proposed and based on the acyclic dehydration of xylose to furfural [2,37]. In the dehydration of xylose to furfural, hydrogen ions (H^+) protonated with hydroxyl group attached to carbon atom, resulting in transition state with a trivalent, positively charged oxygen atom (first step in Scheme 4). Due to the more electronegative oxygen atom in comparison with carbon atom, the positively charged carbon atom was formed

through the loss of one molecular water (second step in Scheme 4). Subsequently, the two electrons from a neighboring C–O bond were prone to form a double bond (third step in Scheme 4), which leaded to the fission of C–O bond and the migration of a hydrogen atom within the molecule (fourth step), H^+ would further protonate hydroxyl oxygen to cause the liberation of another water molecule (fifth step). The trivalent carbon atom would combine and form a relatively more stable ring structure than a double bond (sixth step). The 1,4-elimination of H^+ would produce furfural in the end (seventh Step).

The acyclic dehydration schemes were subsequently under questions by another dehydration mechanism (Schemes 5 and 6) involved the direct rearrangement of the pyranose structure after protonation and dehydration [38–40]. The difference between these latter schemes depended on the protonation of the oxygen atom (either at C1 or C2 position) [38]. Nimlos et al. [38] performed quantum mechanical modeling on these three schemes to study the energy barriers of the transition states involved and reported that energetics supported intramolecular rearrangement rather than ring-opening of the pyran with the lowest energy barriers. Shafizadeh et al. [39] studied the pyrolysis products of xylan polysaccharides through the thermal cleavage of the glycosidic group and found the formation of furfural. Antal et al. [40] investigated both the open-chain hypothesis and two pyranose rearrangement schemes (Schemes 5 and 6) using a kinetic model. They got the conclusion that the kinetic model constructed for the

Table 2
Comparison of heterogeneous catalysts used in the dehydration of xylose to furfural.

No.	Catalyst	Reaction conditions	Conv.(%)	$Y_{furfural}$ (%)	Refs.
1	MCM-41-SO$_3$H	140 °C, 24 h, water-toluene solvent	91	75.5	[61]
2	ZSM-5 zeolite	200 °C, 0.3 h, water solvent	N.D.	46	[58]
3	PSZ-MCM-41	160 °C, 4h, water-toluene solvent	95	42.8	[65]
4	Nafion-117	150 °C, 2 h, DMSO solvent	91.0	60	[67]
5	Dealumin. HNu-6(2)	170 °C, 4 h, water-toluene solvent	40–90	47	[63]
6	H-mordenite 13	260 °C, 0.05 h, water-toluene solvent	98	98	[59]
7	Zeolite beta	170 °C, 4 h, water solvent	100	77	[57]
8	SO$_4^{2-}$/ZrO$_2$-Al$_2$O$_3$/SBA-15	160 °C, 4 h, water-toluene solvent	98.7	52.7	[66]
9	Amberlyst-15/ Hydrotalcite	100 ºC, 3 h, DMF	72.0	36.7	[68]
10	HCl	170 °C, 15 min, biphasic reactor system	92	76	[69]
11	HCl	170 °C, 20 min, biphasic reactor system	98	78	[69]
12	HCl	170 °C, 30 min, biphasic reactor system	100	71	[69]
13	ChCl-Citric acid	90 °C, 0.5 h	53.4 ± 0.8	8.3 ± 0.2	[70]
14	ChCl-Citric acid	90 °C, 30 min, Co-catalyst (AlCl$_3$·6H$_2$O)	64.3 ± 0.3	15.3 ± 0.2	[70]
15	ChCl-Citric acid	100 °C, 30 min, Co-catalyst (AlCl$_3$·6H$_2$O)	69.8 ± 1.2	22.8 ± 0.4	[70]
16	ChCl-Citric acid	120 °C, 25 min, Co-catalyst (AlCl$_3$·6H$_2$O)	86.1 ± 0.3	36.5 ± 0.3	[70]
17	ChCl-Citric acid	140 °C, 10 min, Co-catalyst (AlCl$_3$·6H$_2$O)	90.5 ± 0.7	49.8 ± 0.4	[70]
18	ChCl-Citric acid	140 °C, 15 min, Co-catalyst (CrCl$_3$·6H$_2$O)	82.1 ± 0.9	44.6 ± 0.2	[70]
19	ChCl-Citric acid	140 °C, 25 min, Co-catalyst (FeCl$_3$·6H$_2$O)	96.1 ± 0.4	58.5 ± 0.1	[70]
20	ChCl-Citric acid	140 °C, 25 min, biphasic reactor system, Co-catalyst (AlCl$_3$·6H$_2$O)	99.8	73.1	[70]
21	ChCl-Citric acid	140 °C, 35 min, biphasic reactor system, Co-catalyst (FeCl$_3$·6H$_2$O)	99.7	71.4	[70]
22	MCM-41	170 °C, 4 h, water and 1-butanol solvent	96.9	44.1	[71]
23	MCM-41	200 °C, 1 h, water and 1-butanol solvent	98.9	39.8	[71]
24	arenesulfonic SBA-15	160 °C, 20 h, water/toluene solvent	99	86	[72]
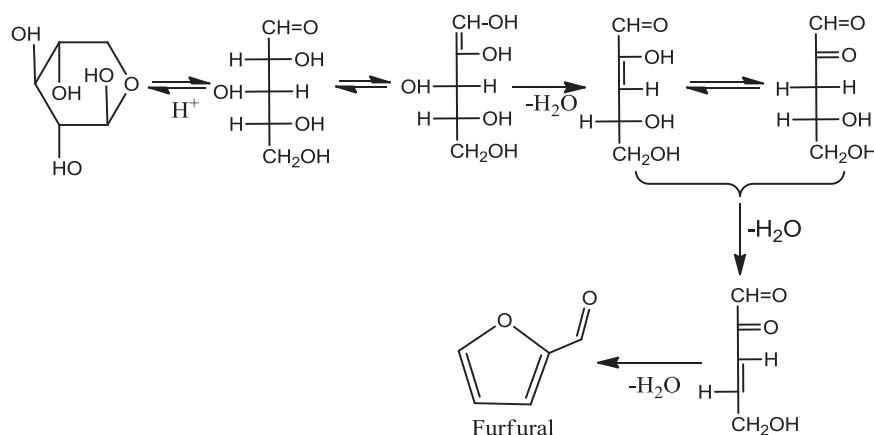
Scheme 3. Production of furfural by dehydrating five-carbon sugars [35,36].

cyclic dehydration mechanism was well matched with the experimental phenomena and further confirmed the latter hypothesis. Albeit a number of studies have performed and investigated the production of furfural, many of these processes and the elucidation of the mechanism are still early in their development, and would benefit greatly from additional research, especially for the *in-situ* studies (e.g., Nuclear magnetic resonance (NMR), Fourier transform infrared spectroscopy (FT-IR), and Isotope technologies) on elucidating reaction kinetics and key mechanistic issues.

4. Production of furfural

In principle, furfural can be obtained from every pentosan-containing material [41–43]. Today, over 280,000 t of furfural is produced every year. The greatest amount was produced in China (200,000 t), followed by the Dominican Republic (32,000 t) and then South Africa (20,000 t) [2]. Together, these three nations account for ~90% of global furfural production. As above-mentioned, furfural is the key platform chemical for both chemical and fuel industries [44–48]. It can replace the diminishing fossil-based

organics for the production of resins, lubricants, adhesives and plastics. It is also widely used to produce value-added chemicals, such as furfuryl alcohol, tetrahydrofurfuryl alcohol, furanoic acid, and tetrahydrofuran [2,3,9,26].

Yield-loss reactions occur when the produced furfural is in the liquid phase environment, especially under the acidic conditions, by the polymerization or by the combination with xylose precursor, leading to low final furfural yield in whole. Major factors affecting furfural yields can be ascribed to fragmentation, decomposition, condensation and resinification as shown in Scheme 7. During the dehydration of xylose to furfural, the fragmentation often occurs to the intermediates and various products will be produced. The formed furfural can undergo further decomposition, condensation between furfural and intermediates, resinification *via* the combination of multiple furfural molecules, thus the total yields of furfural will be greatly reduced. Up to date, different routes and methods have been developed for the production of furfural and tried to reduce the side reactions at most. The first commercial process for furfural production was achieved in 1921 by Quaker Oats [2]. This process employed aqueous sulfuric acid (H$_2$SO$_4$) in a batch mode at 443–458 K to achieve 40–50% yield of

Scheme 4. Acyclic dehydration mechanism from xylose to furfural [37].

Scheme 5. The mechanism of the dehydration of xylose to furfural initially through C1 atom.

Scheme 6. The mechanism of the dehydration of xylose to furfural initially through C2 atom.

Scheme 7. Production of furfural and the possible reactions in the process.
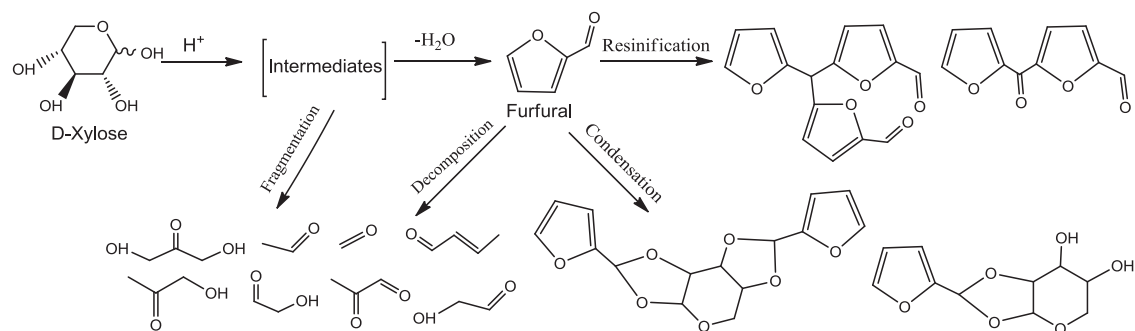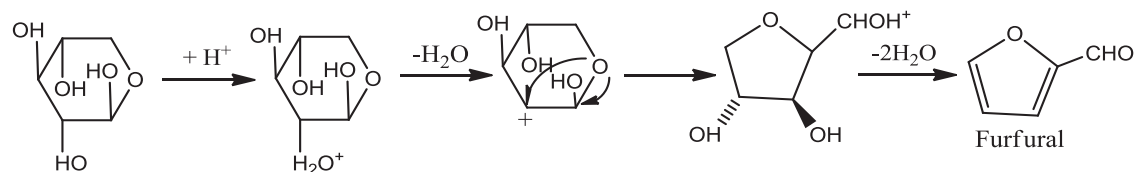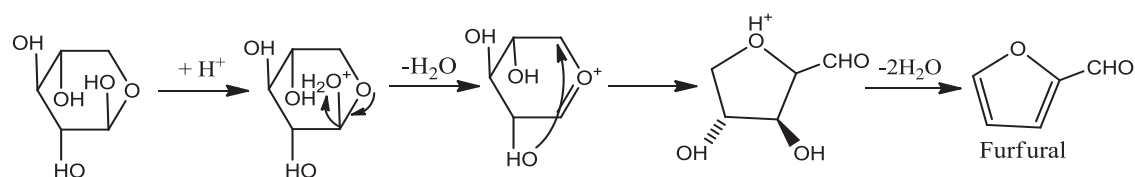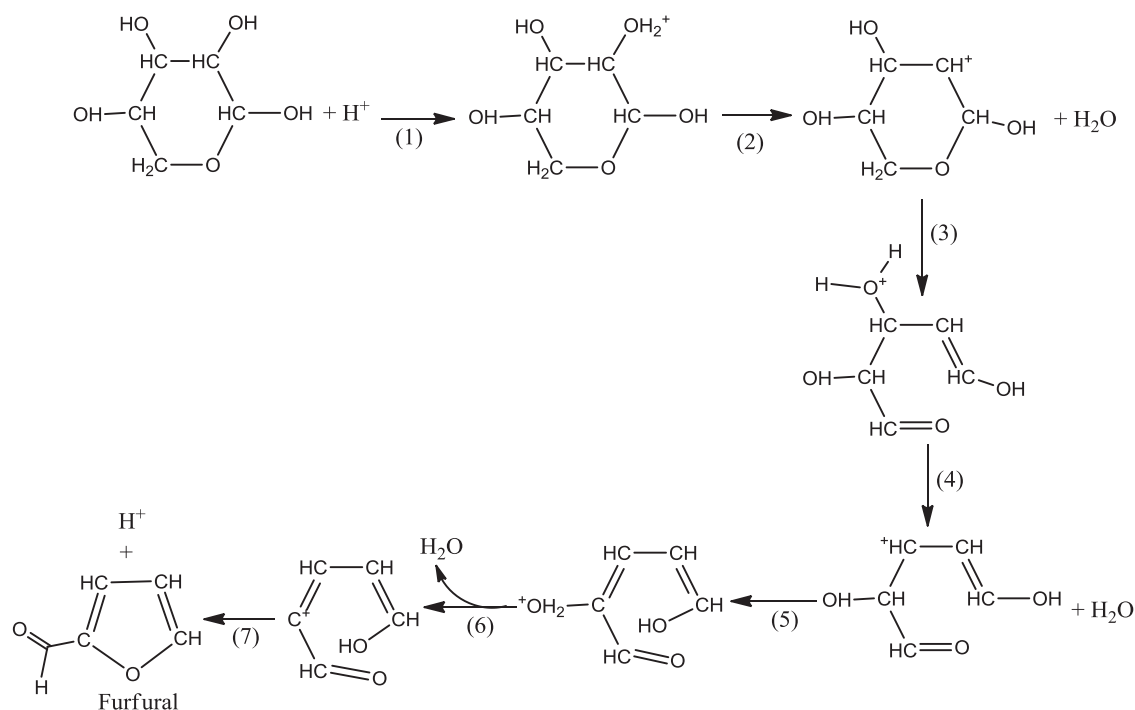
furfural. Following the Quaker Oats process, other furfural production processes were developed in batch or continuous reactor including Westpro-modified Huaxia Technology, Supra yield and Vedernikov's single step furfural production [1–3,9]. However, these commercial processes often utilize mineral acids (e.g., H_2SO_4, HCl) in single phase operation, which associates with the difficulty in the recovery of furfural and the operation or handling of the corrosive mineral acid.

Recently, it was found that the ionic liquids-based process has offered an advantageous route from pentoses and pentosans to furfural. Based on the pioneered study by Binder et al. [49], the conversion of xylose into furfural using the combination of

inorganic salts (e.g., Cr (II) or Cr (III)) and HCl as cocatalyst resulted in moderate yields via isomerization and dehydration. This co-catalyst has been also used for the conversion of xylose and xylan in N,N-dimethylacetamide containing lithium chloride and related solvents [49]. Zhao et al. reported that 63% yield furfural from xylan using CrCl$_3$ catalyst in ionic liquids under microwave-assisted heating at ~200 °C and they also extended this method for the processing of the real biomass corn stalk, rice straw, and pinewood [50]. Potapov et al. [51] developed a method to attach catalytically active centers (Cr and Ti-porphyrin complexes) on the cross-linked polymers that are swellable in the reaction medium (polyacryla-mide gel) with an addition of anhydrous acetic acid to study the dehydration of sugars, this method would allow the xylose dehy-dration at lower temperature with a relatively higher selectivity, but it also results in the formation of a large amount of humins.

Heterogeneous catalysis may provide an efficient methodology for the furfural production, allowing for high reaction rates and high selectivity. Besides, its easy recycle and environmental benign property appeared more attractive for the practical utilizations. For these reasons, the catalytic conversion of pentose to furfural over solid catalysts has received much attention over the last several decades. Moreau et al. [52] have employed the zeolites catalysts (e.g., faujasite and mordenite) to convert xylose to furfural, these porous zeolites catalysts can accommodate a wide variety of cations and can easily be exchanged, high selectivity (90–95%) of furfural at low conversions (< 30%) have been obtained. Valente et al. [57] have investigated the conversion of xylose into furfural using sulfonic acid-functionalized mesoporous silicas catalysts which have large surface areas and narrow pore size distributions. These catalysts have displayed a high furfural selectivity of ~82%. However, the process was slow and took more than 25 h, where the formed carbon deposit aggregated on the surface of the catalyst, resulting in catalyst deactivation through the interaction between reaction substrates or products and acid sites. Besides, different solvent system as well as later biphasic systems as improvement on the production of furfural have been designed [53–55]. Most of solid acid catalysts mainly studied on zeolites [56–59]; microporous and mesoporous niobium silicalites [60]; micromesoporous sulfonic acids [61]; layered titanates, niobates and titanoniobates [62]; delaminated aluminosilicates [63]; cesium salts of 12-tungsto-phosphoric acid and mesoporous silica-supported 12-tungstopho-sphoric acid [64], bulk and mesostructurated sulfated zirconia [65,66], nafion 117 [67] and a combination of different acidic and basic solid catalyst [68], have been applied for the dehydration of xylose to furfural. In general, the results achieved so far in the area of solid catalysis for the production of furfural are quite promising as shown in Table 2, especially in view of the future improvements expected by fine-tuning of the catalyst properties and reaction conditions [69]. In particular, good results have been reported when using zeolites catalysts at relatively high temperature, in terms of furfural selectivity and yield. Future attention may be more focused on the optimization or improvement of these parameters through better design of catalyst and reaction system. Moreover, in view of the industrial implementation of solid catalysts, many aspects are still to be carefully evaluated, like catalysts deactivation and regeneration, water compatibility, mechanical stability, loss and poisoning, and economic cost.

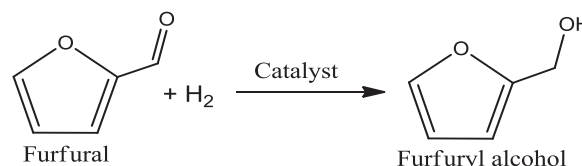## 5. Catalytic hydrogenation of furfural to value-added products

5.1. Furfuryl alcohol

Furfuryl alcohol (FA) is one of the most common products in the hydrogenation of furfural. It has been estimated that ~62% of the furfural produced globally each year is converted into FA.

FA has its largest application in the manufacture of foundry resins [73], where they are often made from cross-linked polymers of FA with itself and other products (furfural, formaldehyde, phenolic compounds, urea, etc.). The resulted resins were shown to possess excellent chemical, thermal and mechanical properties, in addition to withstanding corrosion and solvent action [73]. Owing to its anti-corrosion properties, FA has also been used in the manufac-ture of furan fiber-reinforced plastics for the application in piping, and it is also recommended for high performance chemical processes when chlorinated aromatics, oxygenated organic sol-vents are used [74].

In the last several decades, different types of catalysts and advanced methods have been explored for the production of FA from the hydrogenation of furfural (Scheme 8 and Table 3), one of the most common catalyst was copper chromite catalyst [75–79]. In the past, the commercial production of FA was carried out using 1–2% copper chromite catalyst in the pressure range of 68.9–103.4 bar through the hydrogenation of furfural in 110-gallon autoclaves at 175 °C [75]. Wojcik [78] has also reported the hydrogenation of furan compounds was carried out in the pre-sence of catalysts (e.g., Rany Ni, Cu–CrO) and found that the side reactions were easily occurred when FA was produced. The copper–chromium oxide catalyst yield amounting to 96–99% of theory for FA at 175 °C and the copper–chromium oxide catalyst has little or no effect on the furan ring at 175 °C. Further hydrogenation of FA continued on the copper–chromium oxide catalyst at ~250 °C, slightly higher pressure would produce 2-methylfuran (36%), pentanol (36%), 1,5-pentanediol (15%) and 1,2-pentanediol (14%). The hydrogenation of furfural to FA is relatively easy to achieve and become more mature over the last several decades' development. Future studies should offer a better under-standing of how the catalyst functions and improving the ability of catalysts to deactivate specific classes of compounds, which are beneficial to design the catalytic system under realistic operating conditions.

5.2. Tetrahydrofurfuryl alcohol

Tetrahydrofurfuryl alcohol (THFA) with a molecular formula of $C_5H_{10}O_2$ and a molecular weight of 102 [2,3], is a transparent, mobile, high-boiling liquid with mild odor and is completely miscible with water. It is considered as a green solvent used in agricultural applications, printing inks, industrial and electronics cleaners. The industrial production of THFA is commercially manufactured by Koatsu Chemical Industries in Japan with an annual production volume of ~30 t. On the laboratory level, THFA can be directly produced from furfural or furfuryl alcohol. The conventional THFA is produced by a two-step catalytic hydrogena-tion of furfural via furfuryl alcohol intermediate (Scheme 9) over Cu–Cr and Noble metal catalysts separately [108]. Resasco et al. [89] reported Cu, Pd, and Ni supported on silica catalysts for the hydrogenation of furfural, whereas 5% Ni/SiO$_2$ gave THFA with 5% selectivity at 230 °C. Much higher selectivity of 26% THFA was reported using a homogeneous Ru(II) bis(diimine) catalyst for the direct hydrogenation of furfural [31]. Besides, transition metal-based bimetallic catalysts showed ~4% selectivity of THFA in the hydrogenation of furfural [95]. Supported Ni catalysts are more
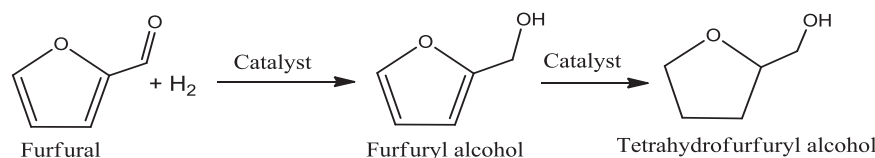

Scheme 8. Hydrogenation of furfural to FA.

Table 3
Representative works from literatures in the hydrogenation of furfural to FA.

No.	Catalyst	Reaction conditions	Conv.(%)	Y_{FA}(%)	Refs.
1	5% Pt/C	175 °C, 80 bar H_2, 0.5 h, n-butanol solvent	99.3	47.9	[80]
2	5% Pt/C	175 °C, 80 bar H_2, 0.5 h, n-decanol solvent	94.5	26.3	[80]
3	5% Pd/C	150 °C, 20 bar H_2, 4 h, acetic acid-assisted	41.2	14.4	[81]
4	5% Pd/Al$_2$(SiO$_3$)$_3$	150 °C, 20 bar H_2, 4 h, acetic acid-assisted	56.9	30.0	[81]
5	5% Cu/Al$_2$(SiO$_3$)$_3$	150 °C, 20 bar H_2, 4 h, acetic acid-assisted	26.1	7.80	[81]
6	5% Ni/Al$_2$(SiO$_3$)$_3$	150 °C, 20 bar H_2, 4 h, acetic acid-assisted	23.9	6.2	[81]
7	Ni–Ce–B	180 °C, 10 bar H_2, 3 h, 30 mL ethanol	96.8	N.D.	[82]
8	Ni–Fe–B	200 °C, 10 bar H_2, 4 h, 30 mL ethanol	100	~100	[83]
9	Cu$_{11.2}$Ni$_{2.4}$–MgAlO	300 °C, 10 bar H_2, 90 mL ethanol	89.9	87.0	[84]
10	5% Pt/C	175 °C, 30 bar H_2, 1 h, 20 mL H_2O solvent, H_3PO_4 (85%)	100	27.0	[85]
11	2% Ir/TiO$_2$	90 °C, 6.2 bar H_2, n-heptane/ethanol	30	30	[86]
12	PtSn/SiO$_2$	100 °C, 8h, 10 bar H_2, 50 mL 2-propanol	~85	~83.5	[88]
13	1% Pd/SiO$_2$	250 °C, H_2/Feed ratio=25, 1 atm H_2, TOS=15 min	69	10	[89]
14	10% Cu/SiO$_2$	230 °C, H_2/Feed ratio=25, 1 atm H_2, 5 min	69	67.6	[89]
15	2 wt% Pt/TiO$_2$/MgO	200 °C, HLSV=2, H_2/furfural=2 mol/mol)	33.6	22.8	[90]
16	MoNiB/γ-Al$_2$O$_3$	80 °C, 3 h, 50 bar, methanol solvent	99.1	90.2	[91]
17	Cu–MgO–Cr	200 °C, 6 h, H_2/furfural=2.5, GHSV=0.05 mol h^{-1} g catalyst^{-1}	71.6	71.6	[92]
18	Cu–Cr	300 °C	60	21–42	[93]
19	Ni$_{74.5}$ P$_{12.1}$ B$_{13.4}$	250 psi H_2, 80 °C, furfural/ethanol=2 mL/170 mL	~95	~77.9	[94]
20	PtSn$_{0.2}$/SiO$_2$	100 °C, 8 h, 10 MPa H_2, 50 mL of propan-2-ol solvent	100	96	[95]
21	1 wt% Pt/ SiO$_2$	100 °C, 8 h, 10 MPa H_2, 50 mL of propan-2-ol solvent	46	45.5	[95]
22	2 wt% Ni/SiO$_2$	100 °C, 8 h, 10 MPa H_2, 50 mL of propan-2-ol solvent	31	23.6	[95]
23	Cu–Fe	160 °C, 90 bar H_2, 5 h	91.0	89.5	[96]
24	Cu–Cr	260 °C, 1 bar H_2	53	51.9	[76]
25	Cu/MgO	180 °C, 1 bar H_2, H_2/furfural=2.5, GHSV 0.05 mol h^{-1} g$_{catal}^{-1}$	98	96.0	[87]
26	Cu–Ca/SiO$_2$	130 °C, 1 bar H_2, H_2/furfural=5, LHSV 0.33 mL h^{-1} mL$_{catal}^{-1}$	100	99	[97]
27	CuLa/MCM-41	140 °C, 1 bar H_2, H_2/furfural=5, GHSV 0.087 mol h^{-1} g$_{catal}^{-1}$	98	> 97	[98]
28	Cu–MgO	180 °C, 1 bar H_2, H_2/furfural=2.5, GHSV 0.05 mol h^{-1} g$_{catal}^{-1}$	98	96	[99]
29	Cu–Cr/TiO$_2$	140 °C, 1 bar H_2, H_2/furfural=3, GHSV 0.04 mol h^{-1} g$_{catal}^{-1}$	90	79.2	[100]
30	Pt/TiO$_x$–V$_2$O$_5$–SiO$_2$	150 °C, 1 bar H_2, H_2/furfural=2, LHSV 2 g h^{-1} g$_{catal}^{-1}$	87	79.2	[90]
31	Ir–ReOx/ SiO$_2$	30 °C, 8 bar H_2, 6 h, Water solvent	> 99	> 99	[101]
32	Cu–Zn–Cr–Zr oxide	170 °C, 20 bar H_2, 3.5 h, isopropanol solvent	> 99	> 95	[102]
33	Raney Ni–CuPMo12	80 °C, 20 bar H_2, 1 h, ethanol solvent	98	97	[103]
34	Co–Mo–B alloy	100 °C, 10 bar H_2, 3 h, ethanol solvent	> 99	> 99	[76]
35	Pt–Sn/SiO$_2$	100 °C, 10 bar H_2, 8 h, isopropanol solvent	90	88.2	[82]
36	Ni–Ce–B alloy	80 °C, 10 bar H_2, 3 h, ethanol solvent	97	~97	[104]
37	Ru/C	165 °C, 25 bar H_2, MTHF solvent	91	42.4	[105]
38	Cu: Zn: Cr: Zr (3:2:1:4)	170 °C, 20 bar H_2, 3.5 h, isopropyl alcohol solvent	100	96	[106]
39	Ni–Sn	isopropanol solvent, 30 bar H_2, 110 °C, 1.25 h	72	70	[107]
40	Ni–Sn/TiO$_2$	isopropanol solvent, 30 bar H_2, 110 °C, 1.25 h	> 99	> 99	[107]

N.D.: not exactly defined.

Scheme 9. Hydrogenation of furfural to THFA.

preferred for both hydrogenation of furfural and FA. In the industrial practice, THFA is often produced from FA with various supported Ni catalysts. At moderate temperature of 50–100 °C, both vapor- and liquid-phase processes are economically feasible. At experimental scale, higher THFA selectivity of 38% was possible over a Raney nickel catalyst at the partial furfural conversion of 50% [94]. Recently, Tomishige et al. [109] proposed that the total hydrogenation of furfural to THFA was obtained in two steps: in an initial step involving the conversion of furfural to FA and then in the second step of FA converted into THFA with 94% yield. More recently, Rode et al. [110] reported the complete conversion of furfural with an enhanced selectivity of 95% THFA in a single pot over a Si−MFI molecular sieve supported Pd catalyst (3% Pd/MFI). To better understand the current technologies for the production of THFA, the typical works from literatures have been depicted in Table 4.

In all, optimum THFAL selectivity was either possible in a single-pot or two-step strategy at the partial or perfect conversion of furfural. Future studies may focus more on the structural modification of the catalyst or the support to more highly selective production of THFA from furfural in one-step with ecofriendly system and low-cost.

5.3. 2-methylfuran and 2-methyltetrahydrofuran

2-methylfuran (MF) and 2-methyltetrahydrofuran (MTHF) are both colorless mobile liquids with high solvent power. The chemical properties of MF and MTHF are often comparable to those widely used solvents (e.g., furan and THF). Recently, they are proposed as highly promising biofuel components mixed with gasoline, some of their physical properties are compared with biofuel ethanol and GVL as shown in Table 5. Besides, MF is also often used as solvent and as feedstock for the production of antimalarial drugs (chloroquine), methylfurfural, nitrogen and sulfur heterocycles, and functionally substituted aliphatic compounds [115–119]. For MTHF, it is inversely soluble in water, i.e.,

Table 4
Catalytic hydrogenation of furfural to THFA.

No.	Catalyst	Reaction conditions	Conv.(%)	Y_{THFA}(%)	Refs.
1	NiO/SiO_2	200 °C, 1 bar	15	> 14.9	[76]
2	Ni/SiO_2	140 °C, 1 bar H_2, GHSV = 1.1 mol h^{-1} g catalyst^{-1}, N_2 protecting	> 99	> 93.1	[109]
3	Raney Ni/Al(OH)$_3$	110 °C, 30 bar H_2, 1.25 h, isopropanol solvent	> 99	> 99	[107]
4	$Ni–Pd/SiO_2$	40 °C, 80 bar H_2, 8 h, water solvent	99	95.0	[111]
5	RuO_2	120 °C, 50 bar H_2, 2.5 h, methanol solvent	100	~76	[112]
6	Ni 5132P + Cu V1283	130 °C, 40 bar H_2, 3 h 5 min, methanol solvent	100	97	[112]
7	Ni 473P + Cu V1283	130 °C, 40 bar H_2, 3 h 10 min, methanol solvent	99	95	[112]
8	RuO_2 + Cu V1283	120 °C, 50 bar H_2, 1 h 35 min, methanol solvent	100	86	[112]
9	Pd/C + Cu V1283	120 °C, 50 bar H_2, 3.5 h, methanol solvent	99	28	[112]
10	5% Ru/C	120 °C, 50 bar H_2, 3 h, methanol solvent	99	59	[112]
11	Ni 5132P	130 °C, 40 bar H_2, 4 h 50 min, methanol solvent	66	4	[112]
12	Ru/C	165 °C, 25 bar H_2, 1-Butanol-water solvent	100	16.6	[105]
13	Ru/C	165 °C, 25 bar H_2, MTHF solvent	91	11.2	[105]
14	Ni–Sn	iso-PrOH solvent, 30 bar H_2, 110 °C, 1.25 h.	16	4	[107]
15	1.4% Pt + 1.4%Ru/C	160 °C, 80 bar H_2, 0.5 h, water solvent	100	9.7	[85]
16	3% Pd/C	160 °C, 80 bar H_2, 0.5 h, water solvent	98.4	62.1	[85]
17	$Pd–Ir–ReOx/SiO_2$	50 °C, 2 h, 60 bar H_2, water solvent	> 99.9	78	[113]
18	$Pd–Rh–ReOx/SiO_2$	50 °C, 2 h, 60 bar H_2, water solvent	> 99.9	18.8	[113]
19	$Pt–Li/Co_2AlO_4$	140 °C, 24 h, 15 bar H_2, ethanol solvent	> 99.9	31.3	[114]

Table 5
Properties of the potential fuel components [3,123,124].

Terms	Ethanol	MF	GVL	MTHF
Mass Weight (g mol^{-1})	46.07	82.10	100.12	86.13
Carbon (wt%)	52.2	73.15	60	69.72
Hydrogen (wt%)	13.1	7.37	8	11.70
Oxygen (wt%)	34.7	19.49	32	18.58
Boiling point (°C)	78	64	207	80.3
Melting point (°C)	− 114	− 89	− 31	− 136
Flash Point (°C)	13	− 22	96	− 12
Density (g mL^{-1})	0.789	0.91	1.046	0.854
Solubility in water (mg/mL)	miscible	3	> =1	150
Enthalpy of vaporization (kJ/kg)	912	357	442.36	364.43

the solubility decreases with the increasing temperature. MTHF is recently used as a specialty solvent, mainly as a higher boiling substitute for tetrahydrofuran. MTHF can also be used in the electrolyte formulation for secondary lithium electrodes [116,117] and as a component of alternative fuels [118–122].

In the presence of hydrogen, the vapor-phase hydrogenation of furfural to MF (Scheme 10) has been reported over various supported Noble metal and bimetallic catalysts. The selective conversion of furfural to MF by Cu-based catalysts often operated at high temperature and low pressure. It was shown that the hydrogenation proceeded through the FA as an intermediate [26,93]. Raney-Cu, Cu/Al_2O_3 and copper-chromite showed similar behavior, although the latter was more active and stable. However, the Cu or copper-chromite catalysts are slowly deactivated by coking at low temperature (130 °C) in the process [125]. To maintain the same production rate the reactor temperature is gradually increased to 150 or 160 °C, where MF is produced through the hydrogenolysis of FA. The catalysts were found to deactivate rapidly, but could be regenerated by coke burn off at 400 °C [125–127]. The copper derived catalysts (e.g., Cu–Zn–Al, Cu–Mn–Si) and the carbon-supported Cu–chromite was also reported to be selective for MF, but also got deactivated within a few days [127–130]. These observations were confirmed and elaborated upon in later studies [131]. To benchmark the typical works on the production of MF, some typical works have been summarized in Table 6. Economical operation would require increasing the catalyst stability and an effective regeneration procedure. Ongoing studies are focused on characterizing and optimizing the catalysts used in this process, on elucidating key

mechanistic issues, and on evaluating how the reaction variables control the yields and selectivity.

The typical procedures for the efficient production of MTHF (Scheme 11) existed two routes: (i) hydrogenation through levulinic acid (LA) resource; (ii) hydrogenation of MF. Different homogenous Ru-derived catalysts [132,133], Cu-composites [134,135] and Noble-metal catalysts [136] have been reported for the production of MTHF (Table 7). For example, Fan et al. [135] reported a yield of MTHF as high as 91% based on the γ-valerolactone (GVL) substrate dissolved in ethanol solvent and Cu/ZrO_2 as a catalyst. The Ni-derived catalysts have also been reported to show good performance [137]. The hydrogenation can be performed in the liquid phase under the H_2 pressure or in the vapor phase at atmospheric pressure with the commonly supported Ni catalysts. The single-stage production of MTHF from LA with a Re/Pd on carbon catalyst has been reported in the patent [138]. Although these processes have not been brought to industrial level yet, they display the potential for the conversion of carbohydrate for the production of bulk valuable chemicals [138].

5.4. Furan

The catalytic decarbonylation of furfural at high temperature would lead to the production of furan through the release of a molecule of carbon monoxide (Scheme 12). It often occurred as a side reaction during the hydrogenation and hydrogenolysis of furfural [142]. The traditional method of producing furan from furfural involved the production of the intermediate furoic acid (through the Cannizzaro reaction), followed by decarboxylation to produce furan [143]. Hurd et al. [144] did some pioneered works and have reported the direct production of furan from furfural using the reaction with the fused alkali (yields up to 60%) and the pyrolysis of furfural (yields ~16.5%). Wilson [145] has reported that the decarbonylation of furfural into furan (over 50% yield) was obtained in the presence of nickel gauze catalyst. Lejemble et al. [146] have studied several metal oxide catalysts (iron, zinc, manganese, chromium, etc.) and Noble metal catalysts, they found Noble metal catalysts are mostly preferred to catalyze the decarbonylation reaction. High temperature (300–500 °C) would result in the ring opening of furan into heavy products, resulting in small pieces (e.g., carbon deposit) on the surface of the catalyst and the deactivation [146]. Singh et al. [147] studied the kinetics of the decarbonylation using the catalyst of Pd supported on carbon and alumina, they found that the carbon was a better support.
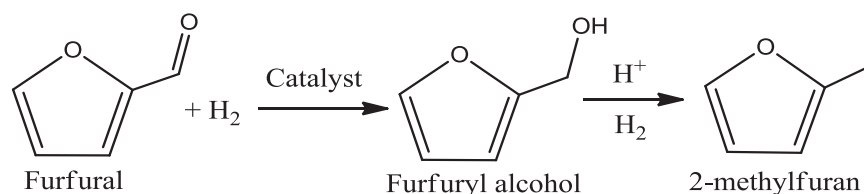
Scheme 10. Hydrogenation of furfural to MF.

Table 6
Representative works on the hydrogenation of furfural to MF using solid catalysts.

No.	Catalyst?	Reaction conditions	Conv.(%)	Y_{MF}(%)	Refs.
1	5% Pt/C	175 °C, 80 bar H_2, 0.5 h, n-butanol solvent	99.3	40.4	[80]
2	5% Pt/C	n-decanol solvent	94.5	23.2	[80]
3	5% Pt/C	n-butanol/water (1:1 vol)	99.7	30.8	[80]
4	5% Pt/C	190 °C, 30 bar H_2, 0.5 h, H_2O solvent	100	3.7	[80]
5	5% Pd/C+$Al_2(SiO_3)_3$	150 °C, 20 bar H_2, 4 h, acetic acid-assisted	69.4	17.9	[81]·
6	5% Pd/C	150 °C, 20 bar H_2, 4 h, acetic acid-assisted	41.2	8.9	[81]·
7	5% Pt/C	160 °C, 30 bar H_2, 1 h, 20 mL H_2O solvent	96.5	4.9	[85]
8	5% Pt/C	175 °C, 30 bar H_2, 1 h, 20 mL H_2O solvent H_3PO_4 (85%)	100	36.6	[85]
9	Cu–Zn–Al	225 °C, 6 h, LHSV=0.7 h^{-1}	99.9	93.0	[128]
10	2 wt% Pt/TiO_2/SiO_2	150 °C, HLSV=2 h^{-1}, H_2/furfural=2 mol/mol)	69.4	18.9	[90]
11	2 wt% Pt/TiO_2/MgO	250 °C, HLSV=2 h^{-1}, H_2/furfural=2 mol/mol)	50.4	5.9	[90]
12	2 wt% Pt/TiO_2/γ-Al_2O_3	200 °C, HLSV=2 h^{-1}, H_2/furfural=2 mol/mol)	33.2	4.7	[90]
13	Cu–Mn–Si	279 °C, 8 h, 1 atm, LHSV=0.49 h^{-1}, n(H_2): n(CHL+FFA)=10:1, coupling reaction	99.8	93.5	[129]
14	Cu/Zn/Al/Ca/Na=59:33:6:1:1	250 °C, LHSV=0.3 h^{-1}, H_2:furfural=25 (molar ratio)	99.7	87	[130]
15	Cu/Zn/Al/Na=59:33:6:1:1	300 °C, LHSV=0.3 h^{-1}, H_2:furfural=25 (molar ratio)	99.7	77.6	[130]
16	Cu/Cr/Ni/Zn/Fe =43:45:8:3:1	200 °C, LHSV=0.3 h^{-1}, H_2:furfural=25 (molar ratio)	99.6	67.0	[130]
17	CuO/$CuFe_2O_4$	220 °C, 90 bar H_2, 14 h	99.4	51.1	[131]
18	CuLa-β zeolite	180 °C, 1 bar, H_2/furfural=5, GHSV 0.087 mol h^{-1} g_{catal}^{-1}	9.5	7.8	[100]
19	Cu–Zn–Al oxide	150 °C, 1 bar, H_2/furfural=10, LHSV 0.3 g h^{-1} g_{catal}^{-1}	99	86.1	[139]
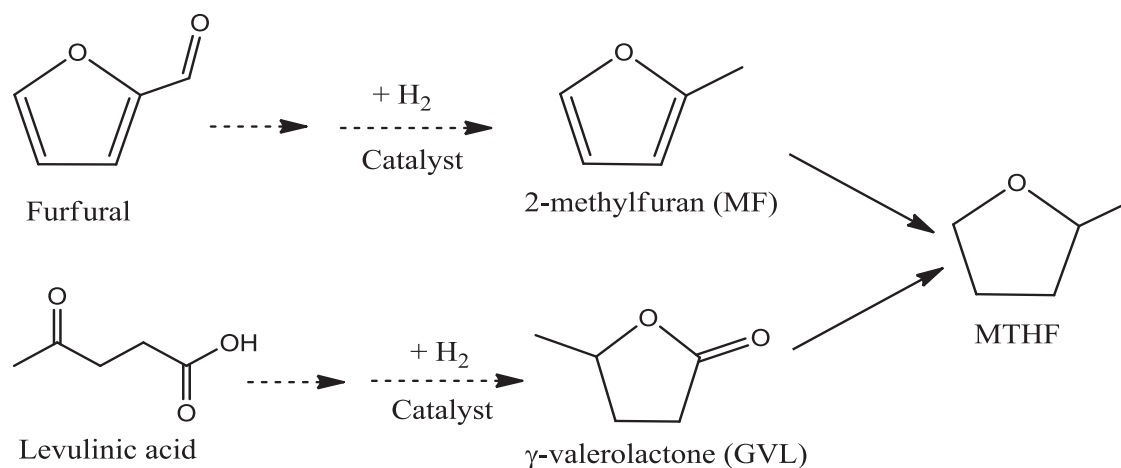
Scheme 11. Production of MTHF from levulinic acid and MF.

Table 7
Catalytic production of MTHF on different solid catalysts.

No.	Catalyst	Reaction conditions	Conv.(%)	Y_{MTHF}(%)	Refs.
1	NiCu/SBA-15	160 °C, 40 bar H_2, 4 h, water solvent	> 99	> 16.8	[140]
2	NiCu/SBA-15	160 °C, 40 bar H_2, 4 h, water solvent, Na_2HPO_4 additive	> 99	> 35.6	[140]
3	NiCu/SBA-15	160 °C, 40 bar H_2, 4 h, water solvent, Na_2CO_3 additive	> 99	> 27.7	[140]
4	3% Pd/C	160 °C, 80 bar H_2, 0.5 h, water solvent	99.8	16.7	[85]
5	5% Pt/C	175 °C, 80 bar, 0.5 h, water solvent	100	9.4	[141]
6	Rh–ReOx/SiO_2	50 °C+120 °C, 2 h+24 h, 60 bar H_2, water solvent	> 99.9	26.9	[113]
7	Pd-Ir–ReOx/SiO_2	120 °C, 24 h, 60 bar H_2, water solvent	> 99.9	11.9	[113]
8	Pd-Ir–ReOx/SiO_2	40 °C+120 °C, 2 h+24 h, 20 bar H_2, water solvent	> 99.9	12.5	[113]
9	5% Pd/C	175 °C, 80 bar H_2, 1 h, water solvent	100	35.6	[80]
10	5% Ru/C	175 °C, 80 bar H_2, 1 h, water solvent	100	6.1	[80]
11	CoMnCr	175 °C, 80 bar H_2, 0.5 h, water solvent	100	16.5	[80]
12	Raney Ni Actimet C	160 °C, 30 bar H_2, 1 h, water solvent	100	23.4	[80]

Besides, Singh et al. [147] also found that the presence of hydrogen enhanced the furan yield and promoted the transport process of commuting the reactants and products to and from the catalyst active sites.

Furan is commercially produced by heating furfural to 158 °C in the presence of 5% Pd catalyst supported on microporous carbon, with potassium carbonate as cocatalyst to promote the reaction. Over 98% furan yields are produced [2]. For the other representative works on the furan production, it has been summarized and depicted in Table 8.

5.5. Tetrahydrofuran

One of the most attractive utilization of furan leans on its conversion into tetrahydrofuran (THF), which holds wide applications as a solvent for numerous chromatographic techniques (e.g., Gel Phase Chromotography) and specialty syntheses which involve complex catalysts and Grignard reagents [2,3,14]. THF is also a preferred precursor for anionic polymerization. For example, THF is polymerized under strongly acidic conditions to form polytetramethylene ether glycol which is used extensively to manufacture urethane elastomers and fibers [3,152]. Besides, THF have been also employed as adhesives, PVC cements, vinyl films and cellophane [153,154].

THF is manufactured by the catalytic hydrogenation of maleic anhydride according to a process patented by du Pont [155]. On the laboratory level, THF is often produced by the cyclodehydration of 1,4-butanediol or hydrogenation of furan. Production of THF (Scheme 13) from furan (ultimately from furfural) would be highly promising alternative to utilize the renewable resources. The hydrogenation reaction has been performed on Noble metals

and Ni-derived catalysts [2]. The hydrogenation of furan is catalyzed by the same catalyst (Pd supported on carbon) used for the decarbonylation of furfural [3]. Good performance has been reported. However, Ni-catalysts are prone to be more attractive than Noble metal catalysts, which was possible due to easy hydrogenolysis side products on the latter catalyst and relatively low cost [2]. At present, one of the biggest issues for the production of THF from furfural is the high yield of coke produced during the process. Although this coke has some value as a source of process heat, it detracts from the total possible yield of THF and also deactivates the catalyst (like Ni/zeolite). The coke formed has high carbon content and is deficient in hydrogen, suggesting that the addition of a hydrogen donor could be useful in limiting the amount of coke produced during the process.

5.6. Other value-added chemicals

There are many other products (e.g., 1-butanol, 1,5-pentanediol, cyclopentanol, cyclopentanone, dihydropyran and butane) that can be produced from the transformation of furfural [140,141,156]. Here, we mainly stated two relatively more attractive products (i.e., cyclopentanol and cyclopentanone). Cyclopentanone is a colorless liquid organic compound with a characteristic strong odor. It is an important chemical intermediate to produce pharmaceuticals, insecticides and rubber chemicals [140]. The production of cyclopentanone is often produced through decarboxylation of adipic acid at high temperature [157]. Recently, Hronec et al. reported that the Pt, Pd, Ni, and Ru catalysts could convert furfural into cyclopentanone through the hydrogenation [80,85,141]. Among them, Pt supported on Al_2O_3 catalyst display 44.7% yield at 97.7% conversion of furfural at the conditions of 175 °C, 80 bar H_2, 0.5 h in water solvent. To more clearly present the current technologies on the production of cyclopentanone, typical works have been depicted in Table 9. Since the reaction pathway is clear, the future work should be more devoted to the development of more stable and cheaper catalyst with high performance.

Cyclopentanol is a colorless liquid organic solvent, it is often used as a perfume and pharmaceutical solvent and as an intermediate for dyes, pharmaceuticals [105]. It is often produced from furfural using the Noble-metal catalysts (e.g., Pt/C and Ru/C)
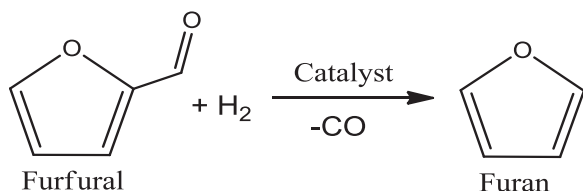
Scheme 12. Hydrolysis of furfural to furan.

Table 8
Catalytic production of furan on solid catalysts.

No.	Catalyst	Reaction conditions	Conv.(%)	S_{furan}(%)	Refs.
1	HZSM-5	300 °C, GHSV=2412 h^{-1}	100	16.5	[148]
2	HZSM-5	400 °C, GHSV=2412 h^{-1}	100	30.6	[148]
3	HZSM-5	500 °C, GHSV=2412 h^{-1}	100	19.5	[148]
4	Pd/HY	350 °C, 1 bar	50	> 99	[76]
5	Pd/SiO$_2$	230 °C, 1 bar, H$_2$/furfural=25, W/F 0.2 h	74	65	[149]
6	Ni/SiO$_2$	230 °C, 1 bar, H$_2$/furfural=25, W/F 4.8g$_{catal}$ mol^{-1} h	72	~43.1	[89]
7	Pt/Ta$_2$O$_5$	700 torr H$_2$ with a balance of He (1300 h^{-1} GHSV, 200 °C).	n.a.	93.8	[150]
8	Pt/SiO$_2$	700 torr H$_2$ with a balance of He (1300 h^{-1} GHSV, 200 °C)	n.a.	92.0	[150]
9	Pt/Al$_2$O$_3$	700 torr H$_2$ with a balance of He (1300 h^{-1} GHSV, 200 °C)	n.a.	90.6	[150]
10	Pt/TiO$_2$	700 torr H$_2$ with a balance of He (1300 h^{-1} GHSV, 200 °C)	n.a.	79.4	[150]
11	Pd/MB-1500	100 °C, 0.75 h, formic acid as hydrogen resource, water solvent	45	77.8	[151]
12	Pd(TOP)/MB-1500	100 °C, 0.5 h, formic acid as hydrogen resource, water solvent	75	26.7	[151]
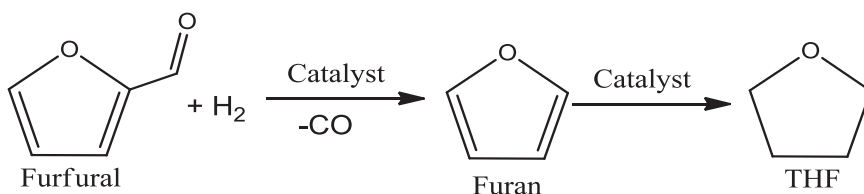
Scheme 13. Hydrogenation of furfural to THF.

Table 9
Catalytic conversion of furfural to cyclopentanone on solid catalysts.

No.	Catalyst	Reaction conditions	Conv.(%)	Y_{CON}(%)	Refs.
1	Ru/C	165 °C, 25 bar H_2, cyclohexane–water solvent	100	17.7	[105]
2	Ru/C	165 °C, 25 bar H_2, 5 h, water solvent	>99	~11	[105]
3	Pt/C	175 °C, 80 bar H_2, 1 h, water solvent	>99	40.2	[80]
4	Pd/C	160 °C, 30 bar H_2, 1 h, water solvent	97.8	67.1	[80]
5	Ru/C	175 °C, 80 bar H_2, 1 h, water solvent	100	57.3	[80]
6	CoMnCr	175 °C, 80 bar H_2, 0.5 h, water solvent	100	7.6	[80]
7	RaneyNi Actimetc	160 °C, 30 bar H_2, 1 h, water solvent	100	17.5	[80]
8	NiCu/SBA-15	160 °C, 40 bar H_2, 4 h, water solvent	~100	~62	[140]
9	NiCu/SBA-15	160 °C, 40 bar H_2, 4 h, water solvent	46	17.9	[140]
9	1% Pt/Al_2O_3	175 °C, 80 bar H_2, 0.5 h, water solvent	97.7	44.7	[85]
10	1.4% Pt/C	160 °C, 80 bar H_2, 0.5 h, water solvent	99.6	43.9	[85]
11	G-134 A	175 °C, 80 bar H_2, 0.5 h, water solvent	99.0	49.0	[85]
12	NiSAT® 320 RS	175 °C, 80 bar H_2, 0.5 h, water solvent	98.3	61.0	[85]
13	Pt/C	160 °C, 30 bar H_2, 0.5 h, D_2O solvent	100	76.5	[85]
14	Pt/C	160 °C, 30 bar H_2, 1 h, water solvent	96.5	51.1	[85]
15	Pt/C	175 °C, 80 bar H_2, 0.5 h, water solvent	100	40.2	[141]

Table 10
Catalytic conversion of furfural to cyclopentanol on solid catalysts.

No.	Catalyst	Reaction conditions	Conv.(%)	Y_{COL}(%)	Refs.
1	Ru/C	165 °C, 25 bar H_2, water solvent	100	16.4	[105]
2	Ru/C	165 °C, 25 bar H_2, MTHF-water solvent	100	47.2	[105]
3	Ru/C	165 °C, 25 bar H_2, Cyclohexane–water solvent	100	21.3	[105]
4	Ru/C	165 °C, 25 bar H_2, 5 h, water solvent	>99	~16	[105]
5	Pt/C	175 °C, 80 bar H_2, 1 h, Water solvent	>99	~36	[80]
6	CoMnCr	175 °C, 30 bar H_2, 0.5 h, water solvent	100	16.4	[80]
7	Raney Ni Actimetc	160 °C, 30 bar H_2, 1 h, water solvent	100	40.0	[80]
8	1.4% Pt/C	160 °C, 80 bar H_2, 0.5 h, water solvent	99.6	16.2	[85]
9	G-134 A	175 °C, 80 bar H_2, 0.5 h, water solvent	99.0	17.7	[85]
10	NiSAT® 320 RS	175 °C, 80 bar H_2, 0.5 h, water solvent	95.4	4.8	[85]
11	5% Pt/C	160 °C, 30 bar H_2, 1 h, water solvent	96.5	3.7	[85]
12	5% Pt/C	175 °C, 80 bar H_2, 0.5 h, water solvent	100	36.2	[141]

[80,105,141] and the highest yield of 47.2% was achieved on Ru/C catalyst under the conditions of 165 °C, 25 bar H_2 in MTHF and water solvent [105]. The typical works on the production of cyclopentanol from furfural have been summarized in Table 10. In all, the yield of cyclopentanol is still low and future development of high efficient, stable and economical catalysts, especially for one-step conversion, will be highly desired.

6. Future prospects

So far in this review, we have outlined the discussion on the production of furfural from hydrolysis of lignocellulosic biomass and critically reviewed the various strategies used for the transformation of furfural to various fuel additives and chemicals. Some examples are given to address the existed issues. Given this, there is a substantial demand for additional researches to study and improve their economics in an effort to support a sustainable biofuel industry.

1. The mineral acid (e.g., HCl, H_2SO_4) catalyzed the production of furfural from xylose should be replaced by an eco-friendly and sustainable process [158]. Ongoing studies should devise a novel catalytic system whereby the renewable and non-edible feedstocks (e.g., hemicellulose) should be utilized and highly selectively transformed into furfural.
2. Future improvements are expected by fine-tuning of the catalyst properties and reaction conditions to enhance the yield of furfural and the yield of the desired products from the conversion of furfural [69]. The reusable catalysts prepared from inexpensive, Earth-abundant materials that can quantitatively convert lignocellulose solids to furfural via a one-pot reaction will be more desired [159,160].
3. The catalysts developed should fully use a variety of catalytic functions, including acid sites, basic sites, and metal hydrogenation sites, to accomplish the common goal of selectively removing oxygen functional groups [161]. By identifying and tuning important catalyst parameters, more effective catalytic materials are designed with improved selectivity to desirable products and increased rate of reaction. Future attention may also more focus on the catalysts deactivation and regeneration; mechanical stability; and economic viability [162].
4. The studies on the conversion of furfural to fuels and chemicals, some are still at early development like the production of fuel 2-methylfuran and 2-methyltetrahydrofuran. Future studies of the lab-scale reactor experiments should pay more attention to identify important catalyst parameters which have determining effects on the rate of catalytic reactions and the selectivity towards desirable products [162,163].

We hope that the concepts described herein might be useful for future development of new, economically viable routes for the catalytic conversion of furfural to fuels and chemicals.

7. Concluding remarks

The development of sustainable technologies for the production of carbon-based chemicals and alternative fuels from the renewable resource biomass has gained tremendous importance. Biomass, being an overfunctionalized starting material, requires selective oxygen removal reactions (e.g., hydrogenation,

dehydration, hydrogenolysis etc.) to obtain platform chemicals (e. g., levulinic acid, furfural etc.) selectively, on which biorefining strategies can be established. In addition, the presence of an aqueous/condensed phase environment and the formed coke from side reactions in the biomass-related conversion reactions present challenges for the utilization of traditional catalysts. Different solid acidic or functionalized catalysts (zeolite, mesoporous materials, and layered hydrotalcite) should be more developed for the efficient production of furfural. They offer the potential for simplicity of operation, easy recycle and environmental benignity. The acid properties and pore geometry are reported to be the most important properties of the microporous and mesoporous catalysts. An examination of the effects of the process parameters is also very important for optimizing the composition of the product. In particular, it is very important to develop methods that prevent catalyst deactivation. It may be also desirable in specific applications to employ chemical processing steps to directly convert the C5 sugars in hemicellulose through furfural intermediate to fuels and/or chemicals.

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